

Mesoscopic fluctuations in superconducting dots at finite temperatures

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We study the thermodynamics of ultrasmall metallic grains with the mean level spacing δ comparable or larger than the pairing correlation energy in the whole range of temperatures. A complete picture of the thermodynamics in such systems is given taking into account the effects of disorder, parity and classical and quantum fluctuations. Both spin susceptibility and specific heat turn out to be sensitive probes to detect superconducting correlations in such samples.

Superconducting coherence is expected to be completely washed out in small metallic grains, where the average level spacing $\delta \sim 1/(\mathcal{N}(0)V)$ may be comparable or even larger than the BCS energy scale Δ [1]. Despite of that, a series of experiments [2,3] by Ralph, Black and Tinkham (RBT) revealed a gap related to superconductivity in individual nanosized metallic grains, $\delta \lesssim \Delta$, with large electrostatic energy fixing the total number N of electrons. The BCS description of superconducting coherence is no longer valid and the characterization of “superconductivity” from the bulk to the ultrasmall-grain regime has been studied in recent theoretical works [4–7]. Starting from the standard pairing Hamiltonian [3], several spectral features at $T = 0$ were calculated, which turn out to be universal functions of the single scaling parameter δ/Δ [5]. It is remarkable that pairing determines strong fluctuational “superconductivity” even in ultrasmall grains [4], where $\delta \gtrsim \Delta$ (we call this the “dot” regime). As in micron-size samples [8], parity effects are present, i.e. physical properties depend on N being odd or even. An exact solution for the pairing problem in finite systems was found long ago by Richardson and Sherman (RS) [9].

In this work the thermodynamics of an *ensemble* of monodispersed superconducting dots is studied. The specific heat $c_V(T)$ (see Fig. 1) and the spin susceptibility $\chi(T)$ (see Fig. 2) are obtained in the whole temperature range. Our work is motivated by the fact that thermodynamic properties are a unique experimental tool in detecting unambiguous traces of superconducting correlations in the dot regime, where tunneling spectroscopy on *individual* dots is not sensitive enough [2]. Di Lorenzo et al. [10] proposed that a possible signature of pairing for $\delta \gtrsim \Delta$, is the reentrant behavior of the spin susceptibility $\chi_o(T)$ in dots with odd N , which is due to the combined parity and interaction effects, using a simple equally spaced spectrum for the single particle energies.

In ensembles of grains the single-particle spectrum is statistically distributed and characterized by level repulsion [11]. The statistics has a universal character due to general symmetry properties and is described by Random Matrix Theory (RMT). The thermodynamics of ensem-

bles of normal metal grains was studied long ago [12], but only in recent years the first experimental evidence of mesoscopic fluctuations and level repulsion in normal metal grains was provided with the observation of the T^2 -dependence of the specific heat and of other thermodynamic quantities [13]. Pioneering experimental works on thermal properties of small superconducting grains date back to the 80s [14].

Concerning superconductors, level statistics was found to yield enhanced superconductivity and parity effects in micron-size samples [15]. Similar results have been recently found also in the dot regime [16] at $T = 0$. Here we focus on ensembles of dots at finite temperature. They exhibit detectable features characteristic of the interplay between pairing interaction and the universal statistics of mesoscopic fluctuations, which determines the physics.

Our starting point is the Hamiltonian

$$\mathcal{H} = \sum_{\alpha,\sigma} (\epsilon_\alpha - \sigma \mu_B H) c_{\alpha,\sigma}^\dagger c_{\alpha,\sigma} - \lambda T^\dagger T, \quad (1)$$

where α spans a shell of Ω pairs ($\sigma = \pm$) of single particle energy levels with statistically distributed energies ϵ_α and annihilation operator $c_{\alpha,\sigma}$. The magnetic field H enters in the Zeeman form (μ_B is the Bohr magneton). For $H = 0$ the pair of states $\sigma = \pm$ are degenerate and time-reversed. The operator $T = \sum_{\alpha=1}^{\Omega} c_{\alpha,-} c_{\alpha,+}$ appears in the interaction term, which scatters pairs with amplitude λ , so a pair of levels $\sigma = \pm$ occupied by a single electron is blocked [3]. Relevant energy scales are the average level spacing δ and the BCS energy, defined as $\Delta = \Omega \delta / [2 \sinh(\delta/\lambda)]$. This model stems from a rather general description of electron-electron interaction in the metallic regime (large dimensionless conductance, $g = E_T/\delta \gg 1$, where E_T is the Thouless energy) which has been recently proposed [17]. The Hamiltonian Eq.(1) describes universal properties of pairing interaction in disordered metallic dots, with fixed N and negligible exchange interaction. We assume that the energies ϵ_α are distributed according to the Gaussian Orthogonal Ensemble (GOE), which describes mesoscopic fluctuations when no spin-orbit interaction is present and time-reversal symmetry is preserved [11].

Level statistics has a drastic effect if $T \ll \delta$, where the thermodynamics is determined by samples with δ_1 , the closest level spacing to the Fermi energy, much smaller than the average δ . The relevant excitations involve only few levels around the Fermi energy, and excitation energies can be estimated by solving the problem in a small shell, $\Omega' \ll \Omega$, with renormalized coupling constant $\lambda \equiv \tilde{\lambda}_\Omega \rightarrow \tilde{\lambda}_{\Omega'}$ [4,6,10]. Let's consider dots with even N and estimate the leading low temperature contribution to $c_{Ve}(T)$. In the regime $\delta \gg \Delta$, the system is first renormalized to an effective one with two electrons in two doubly degenerate levels, and interaction $\tilde{\lambda}_2$. We have to consider six states, and the relative excitation energies: ground state, excited state of paired electrons ($\tilde{E}_p(\delta_1) = 2(\delta_1^2 + \tilde{\lambda}_2^2)^{1/2}$) and four states corresponding to a broken pair with different spin configurations ($\tilde{E}_{bp}(\delta_1) = \tilde{\lambda}_2 + \tilde{E}_p(\delta_1)/2$). Notice that even if the coupling is weak, $\tilde{\lambda}_2 \ll \delta$, dominant configurations have $\delta_1 \lesssim \tilde{\lambda}_2$. The response of a set of grains is evaluated by retaining only fluctuations of δ_1 , governed by the level spacing distribution $P_1^{\text{GOE}}(\delta_1)$. In this way we obtain the analytic form for $T \ll \delta$. The leading term for $T \ll \tilde{\lambda}_2$ reads

$$c_{Ve}(T) = 3\pi^2 \frac{\tilde{\lambda}_2^3}{\delta^2 T} e^{-\frac{2\tilde{\lambda}_2}{T}} \quad (2)$$

and shows a gap $2\tilde{\lambda}_2$. In the limit $\tilde{\lambda}_2 \ll T \ll \delta$ the full analytic result reproduces the known result for normal metal grains [12]. For $c_{Vo}(T)$ we have to consider an effective three (fluctuating) level problem, and we obtain

$$c_{Vo}(T) = \frac{3}{2}\pi^2 \zeta(3) \left(\frac{T}{\delta}\right)^2 + O\left(\frac{\tilde{\lambda}_3}{\delta}\right)^2, \quad (3)$$

which shows no trace of a gap. The contribution of superconducting correlations for $T \ll \tilde{\lambda}_3$ is a correction of the result for normal grains [12], because the most important low-energy excitations are obtained by moving the unpaired electron.

Dots at intermediate temperatures can be studied numerically by the massive use of the RS exact solution. Noninteracting random spectra are obtained by diagonalizing 500×500 random matrices belonging to the GOE and taking the central levels of the resulting semicircular distribution, in order to prevent undesired border effects. For each disorder realization we evaluate the partition function from the universal Hamiltonian Eq.(1) using the RS solution and calculate the average free energy. For the curve $\delta/\Delta = 50$ shown in Fig. 1 we used sets of 50 levels. At intermediate temperatures ($T \lesssim 0.25\delta$ for the curve in Fig. 1) we used 500 realizations and an energy cutoff 5δ . At larger coupling λ , corresponding to the crossover region $\delta/\Delta \gtrsim 1$, and when excited states with random spectra are concerned, singularities in the RS equations become untractable. Then the low-temperature behavior for $\delta/\Delta \gtrsim 1$ shown in Fig. 1 was studied following

Ref. [6]: for each realization of disorder and configuration of blocked levels the interaction is scaled down to some low-energy cutoff and the effective small (≤ 12 levels) system, and is then diagonalized.

Both methods described above cannot be used to obtain results at temperatures $T \sim \delta, \Delta$ where $c_V(T)$ is expected to show anomalies. In this regime a huge number of states (at least $5 \cdot 10^4$ already at $T \sim \delta$) are needed for *each* single disorder realization. Then for high temperature we use a functional technique in the parity-projected (PP) grand canonical ensemble. Following Janko et al. [8] we introduce the even and odd N partition function

$$Z_{e/o}(T, \mu) = \frac{1}{2} \sum_{N=0}^{\infty} e^{\mu N/T} [1 \pm e^{i\pi N}] Z(T, N), \quad (4)$$

for each given realization of disorder. Here $Z(T, N)$ is the canonical partition function so $Z_{e/o}(T, \mu)$ involve only sectors where N is not fixed but its parity is. The effective imaginary-time action is obtained from Eq.(1) in the standard way and $Z_{e/o}(T, \mu)$ can be expressed as a path integrals over a Hubbard-Stratonovic (HS) auxiliary field $\Delta(\tau)$ [10]. This non-linear functional integral is evaluated in the RPA', an approximation which has been widely employed to study the Anderson model [18]. We extract the static part of the HS field in the Matsubara-Fourier representation, $\Delta(\tau) = \Delta_0 + \sum_{n \neq 0} \Delta(\omega_n) \exp(-i\omega_n \tau)$, evaluate quantum corrections by including the contribution of small-amplitude deviations around a generic static path Δ_0 and perform numerically the remaining ordinary integral over Δ_0 . We used systems of 100 levels distributed according to GOE. Finally the resulting free energy is averaged over 400 samples. Results for $c_{Ve}(T)$ are shown in Fig.1. For large enough - albeit still nano-sized - grains a finite temperature anomalous enhancement develops, which can be attributed to the presence of pairing interactions.

We now study the spin susceptibility. Using the same arguments leading to Eqs.(2,3) we can conclude that at low temperatures the susceptibility of grains with even N is exponentially suppressed, so we concentrate on $\chi_o(T)$. For equally spaced single particle spectrum $\chi_o(T)$ shows a reentrant behavior for non-vanishing pairing interaction, because at low temperature the leading contribution is the $1/T$ Curie-like coming from the unpaired electron, whereas the response of the paired electrons exponentially increases with T and becomes dominant at larger temperatures [10]. As compared with results for equally spaced spectra, we notice that level statistics triggers two competing effects: the availability of low-lying excitations tends to increase $\chi_o(T)$, which would wash out the reentrance; on the other hand disorder enforces superconductivity, which would determine the opposite trend.

We evaluate $\chi_o(T)$ using the PP partition function Eq.(4) in the RPA'. Results (Fig. 2) clearly show that

$\chi_o(T)$ is reentrant also in disordered samples. The reentrance is slightly less pronounced than for regular spectra and it is present always but for unphysically small grains. Notice that the “superconducting” $\chi_o(T)$ is well suppressed with respect to normal metal grains, confirming the expectation that disorder favors superconductivity. The leading behavior of $\chi_o(T)$ for $T \ll \delta$ is unaffected by level statistics.

We now discuss experimental signatures of superconducting correlations. The main point is that in ensembles of dots available in experiments roughly 50% have odd N and 50% have even N . At low temperatures the effect of pairing is detectable in the total $c_V(T)$: in an ensemble of normal metal grains the relative contributions to the ensemble specific-heat of dots with even N is about 63% [12]. Pairing suppresses this contribution, Eq.(2), whereas in practice it does not affect $c_{Vo}(T)$, Eq.(3). Thus pairing reduces the total $c_V(T)$ of $\sim 2/3$. Another signature is that $c_V(T)$ increases with an applied magnetic field. Other signatures can be found at intermediate T : The total susceptibility $\chi(T)$ is expected to show reentrant behavior ($\chi(T) \approx \chi_o(T)$, since $\chi_e(T)$ is exponentially suppressed), except for extremely weak interactions or extremely small grains. Another signature is the *increase* of $\chi(T)$ with the applied magnetic field. In the same temperature regime ensembles of dots with $\delta/\Delta \sim 1$ show an anomalous enhancement arising from the contribution of $c_{Ve}(T)$ which can be shifted towards lower temperatures and the progressively suppressed by applying a magnetic field. The whole phenomenology could provide unambiguous evidence of the presence of pairing correlations even in the dot regime.

The procedure used to obtain the analytic results for $T \ll \delta$, neglects fluctuations of the renormalized coupling $\tilde{\lambda}_2$ ($\tilde{\lambda}_3$ for dots with odd N). They arise from fluctuations of larger shells of levels which may be systematically accounted for. In normal metal grains [12], they can be neglected for $T \ll \delta$. We checked numerically that c_{Ve} is exponentially suppressed and that for $\delta/\Delta \gg 1$ the exponent roughly agrees with the scaling form discussed in Ref. [4]. We used a large number of realizations ($\sim 10^4 - 10^5$) since at very low T , the system is very sensitive to the statistic. Detailed account will be given elsewhere.

Some remarks on the results presented above are clearly stated if we draw a comparison with a dot having equally spaced noninteracting levels, $\epsilon_\alpha = \alpha\delta$. In this case all the thermodynamic quantities show gapped behavior for $T \ll \delta$. This is essentially due to the finite level spacing [12,10], for instance the even specific heat has a gap $\delta + \lambda_2$. On the contrary, in ensembles of grains gapped behavior is not the rule. When a gap is present, it is due *only* to the pairing interaction, as in the case of $c_{Ve}(T)$, Eq.(2).

In Fig.(3) we present results at finite temperatures for $c_{Ve}(T)$ and $\chi_o(T)$ for regular spectra, $\epsilon_\alpha = \alpha\delta$. In this

case the exact RS solution allows to reach temperatures slightly larger than δ ; larger temperatures ($T \gtrsim \delta$) were studied by the PP approach, Eq. (4). In the inset we show $\chi_o(T)$, calculated using the canonical RS solution, and the PP grand canonical approach in the RPA' and in the Static Path Approximation (SPA) [10]. In the SPA fluctuations around the static path Δ_0 are neglected when evaluating the PP partition function Eq. (4). The SPA accounts for thermal fluctuations and it has been successfully employed to study the thermodynamics of micrometer size grains [19]. By comparing the SPA with the RPA' results we can quantify quantum corrections. As expected quantum superconducting fluctuations tend to enhance the features of pairing: the reentrance in $\chi_o(T)$ is deepened compared to the SPA result getting closer to the exact result for $T \sim \delta$. Differences between the RPA' and the exact result reflect the different sets of excitations available in the canonical and in the PP grand-canonical ensembles. The discrepancy is small and probably undetectable when pairing interaction is active, so RS solution and RPA' can be used in combination. Small differences are present also in $c_{Ve}(T)$ (Fig.3) and they are expected to persist at $T \gg \delta$. In this latter regime $c_{Ve}(T)$ approaches the behavior of normal metals, where it is known that the canonical $c_V(T)$ is smaller than the grand-canonical one, asymptotically by a quantity $\frac{1}{2}k_B$ [19].

We now focus on the anomaly at intermediate temperatures appearing in $c_{Ve}(T)$. The qualitative behavior of $c_{Ve}(T)$ for $\delta/\Delta \sim 1$ is reminiscent of what observed in bulk superconductors, but this is partly due to the special choice of the equally spaced noninteracting spectrum. In fact the $T \lesssim \delta$ enhancement in the specific heat is present also if the pairing interaction is switched off. This artifact is not present for normal grains with levels ϵ_α distributed according to the GOE statistics (symbols in Fig.3) [12]. Thus the analysis of the effects of level statistics is necessary for a reliable study of the thermodynamics of small grains and gives an unequivocal discrimination of the effects of the pairing interaction.

In summary we studied the thermodynamics of ensembles of ultrasmall superconducting grains, addressing for the first time this problem in the dot regime. We draw a picture of the physics which comes from the interplay of disorder, strong pairing fluctuations and fixed number of electrons in each dot. Thermodynamic properties are a unique experimental tool in detecting unambiguous traces of superconducting correlations in dots. We found that several signatures of pairing (the low and intermediate temperature anomalies of the specific heat and the reentrant spin susceptibility) are experimentally detectable in ensembles of dots, despite superconductivity in the BCS sense breaks down. Finally the low-temperature behavior of $c_V(T)$ may provide direct evidence of the effects of level statistics [13] in interacting metallic systems.

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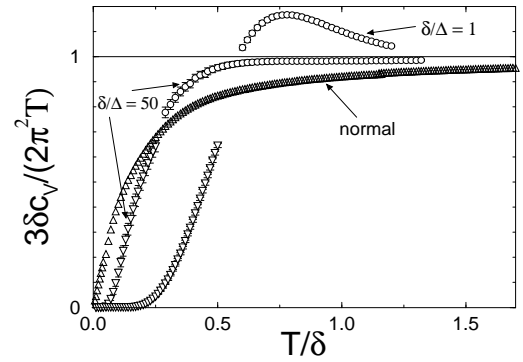


FIG. 1. Rescaled specific heat $c_{v_e}\delta/\gamma T$ vs. temperature in units of δ , disordered case. Circles: the RPA' results; triangles: the exact canonical results.

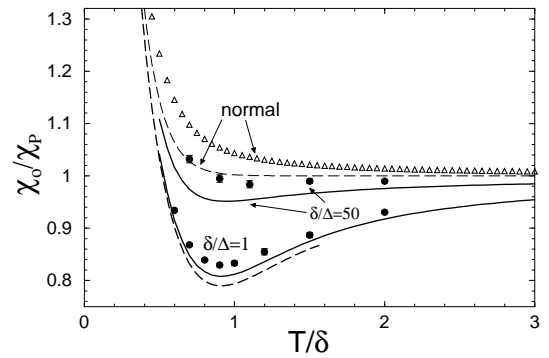


FIG. 2. Spin susceptibility for dots with odd N . Equally spaced noninteracting single-particle levels case as given by the RS canonical solution (dashed lines), and the RPA' (solid), are compared with results for GOE distributed single-particle levels obtained by RPA' (circles) and with the exact canonical calculation (triangles).

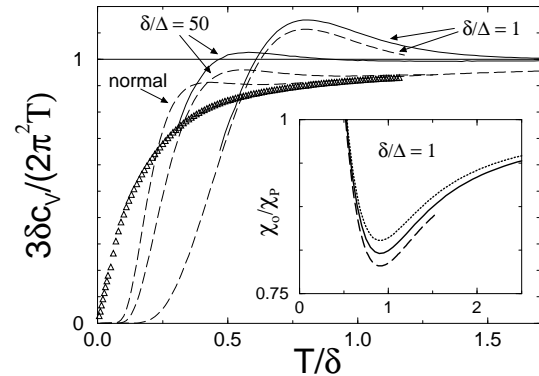


FIG. 3. Thermodynamic quantities for dots with equally spaced spectra, calculated by the RS solution (dashed lines), the SPA (dotted) and the RPA' (solid) as a function of temperature in units of δ . Main figure: the rescaled specific heat $c_{v_e}/\gamma T$. The curve for normal metal disordered dots is plotted for comparison (triangles), see text. In the inset the odd spin susceptibility $\chi_o(T)$, see text.